Section 7

CLEANING AND CORROSION CHARACTERISTICS OF ALCOHOL

Quick Reference Data

Materials Subject to Degradation from High Concentration of Alcohols

- lubricating oils
- terne steel (in gas tanks)
- cylinder walls, fuel pumps, carburetors
- polymers, elastomers, rubbers, plastics (hoses)
- polymethane
- cork gasket material
- leather
- polyester bonded fiberglass laminate

Additives to Prevent Corrosion from Alcohols

- Higher alcohols to minimize phase separation
- Corrosion inhibitors
- Acid neutralizers in lubricants
- Surface treatment of engine parts (nitriding and chrome plating)

Useful Terms and Definitions (also see Glossary)

- **Corrosion:** a gradual wearing away or alteration by a chemical or electrochemical.

- **Formic Acid:** a colorless, pungent liquid acid (HCOOH) that is made by acidification of sodium formate. Formerly obtained from ants, spiders, etc. Synthetically, it is formed in the combustion chamber during the combustion of methanol or water-contaminated ethanol. Also known as methanoic acid.

- **TAME** (Tertiary Amyl Methyl Ether): an ether formed by the reaction of methanol and either isoamylene or isopentalene.

- **Terne Metal:** sheet iron or steel coated with an alloy of about 4 parts lead to 1 part tin.

Key Issues and Implications

Issue #1: Alcohol Combustion Characteristics and Acid Formation

At low engine temperatures, the combustion of methanol (or water-contaminated ethanol) produces water vapor and formaldehyde, which in turn produces formic acid inside the engine.

Implications of Combustion Characteristics and Acid Formation:

The water vapor and formic acid formed during low-temperature combustion of methanol (or other alcohols contaminated with high percentages of water) can oxidize metal engine components and reduce the lubricating ability of engine lubricating oil. Oxidation and reduced lubrication will lead to accelerated wear of engine parts such as cylinder walls, crankshafts, and bearings.

Proposed Solutions:

- Use of acid neutralizers in lubrication oil.
- Surface treatment of engine parts (such as soft nitriding crankshafts or plating cylinder bores with chrome).
- More frequent replacement of lubrication oil or higher quality synthetic oils or a redesign of conventional engine lubrication oils.

Detailed Information: Refer to pages 7-2 through 7-4 and 7-9 through 7-11.

Issue # 2: Alcohol Fuels as Reactive Solvents

Unlike gasoline, alcohols have a fairly strong solvent property that can harm some materials in engine fuel systems; can lead to lubrication failures in engines; and can loosen deposits in gas tanks and pipelines.

Implications of Alcohol's Solvent Capabilities:

- For 10% or less ethanol blends, there are no implications -- all automobiles sold in the U.S. now use fuel system components designed to use this blend under warranty.
- Premature degradation of certain common engine/fuel system materials.
- Reduced lifetimes or lower effectiveness of engine lubricants.
- Loosening of pre-existing deposits in storage tanks and pipelines.

Proposed Solutions:

- Fuel system components must be selected which are immune to the solvent action of alcohols--materials are available that can withstand this solvent action. For fuels containing high percentages of methanol fuel, solutions appear to have been found, although further testing and data is needed to verify performance.
- For higher percentage alcohol (especially methanol) fuels, there are a number of options for preventing corrosion, including: use of stainless steel or anodized aluminum components and the use of "higher alcohols" (those with more carbon in their molecular make-up) additives to act as corrosion inhibitors.
- Further investigation is needed on pipeline maintenance procedures to minimize deposits susceptible to alcohol solvent action.

Detailed Information: Refer to pages 7-4 through 7-9.

Section 7
CLEANING AND CORROSION CHARACTERISTICS OF ALCOHOL

- Solvent Characteristics of Alcohols and Alcohol Blends
- Influence on the Combustion Chamber
- Effects of Alcohols on Various Materials
- Influence on Fuel Distribution System
- Vehicle Failures
- Additives Required to Prevent Corrosion

Introduction

The different chemical structures of alcohol fuels (ethanol or methanol) and gasoline necessitate significant changes to current vehicle technology. A joint research effort by 14 major U.S. oil companies and three of the largest auto companies is currently focusing on experimental and commercial production of flexible fuel vehicles. These are specifically designed to run on high level alcohol blends as well as on conventional petroleum-based fuels. Unfortunately, the reliability and durability of flexible fuel vehicles depends on alcohol solvent and corrosion properties. Unlike gasoline, alcohols are strong solvents and are more highly corrosive. Methanol has been found to be more corrosive than ethanol, both in material degradation and the formation of acid within the combustion chamber, which reduces the effectiveness of the lubricating oil. The solvent effects of alcohol fuels on both the fuel distribution system and vehicle are addressed in this section, as well as the corrosion sensitivity of various metals and non-metals found in current vehicle and fuel distribution systems. Finally, a strategy to minimize the corrosive effects of alcohol fuels is also presented.

Solvent Characteristics of Alcohols and Alcohol Blends

Alcohols, because of their high polarity and the ability to form hydrogen bonds, are used as excellent solvents in the chemical industry. However, this solvent characteristic can cause problems when the alcohol is used as a fuel. These problems may occur in the fuel distribution system as well as in the combustion chamber.

Influence on the Combustion Chamber

A liquid fuel, while burning on a cold surface, can dissolve significant amounts of its combustion products. As discussed earlier, alcohols have much higher latent heats of vaporization than gasoline. Therefore, if the alcohol inducted into an automobile's cylinder is not sufficiently vaporized, the liquid fraction of the alcohol (ethanol or methanol) can act as a solvent for its combustion products. These products are corrosive (including formic acid, for example), degrading the lubricants and greatly increasing wear on cylinder walls.

Combustion residues from neat methanol include water, unburned alcohol, formaldehyde, formic acid, and methylenehydroxy-peroxide. In addition to these constituents, relatively low concentrations of acetaldehyde and acetic acid are found in combustion residues of ethanol, isopropanol, n-propanol and n-butanol. Methanol combustion residues contain substantially higher concentrations of formaldehyde and formic acid than the higher molecular weight alcohols, but all alcohol combustion residues contained about the same levels of methylenehydroxy-peroxide. The concentrations of combustion products in combustion residues, particularly formaldehyde, formic acid and methylenehydroxy-peroxide, tended to increase as the coolant temperature was raised. [1,2,3,4,5]

A number of studies have been undertaken which deal with the corrosion and wear within the engine chamber caused by the use of either methanol/gasoline or ethanol/gasoline blends. [6]

The formic acid and the water formed by the methanol combustion are the principal causes of corrosion and wear. Because the hydrogen-to-carbon or H/C ratio of methanol is higher than that of gasoline, a large amount of water vapor is formed by methanol combustion. Theoretically, 23 mol % of water is formed from methanol combustion compared to 13 mol % of water from gasoline. This explains the increased tendency for water to accumulate in the lubricant oil when the engine is fueled with methanol. At oil and water temperatures of around 40°C (while the engine is warming up), the volume of water condensed from methanol combustion is twice as great as that from gasoline, as illustrated in Figure 7-1. [7]

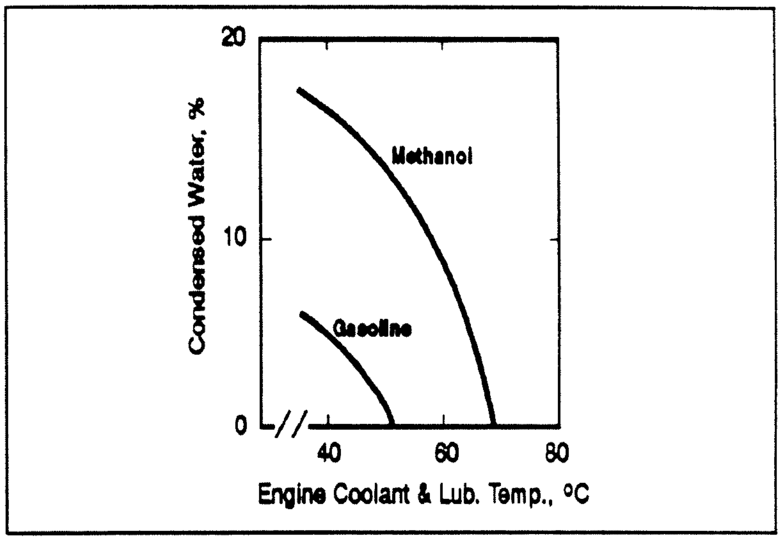

Figure 7-1., Condensed water from methanol and gasoline combustion.

This partial oxidation of methanol produces formaldehyde, which converts easily to formic acid.

$$CH_3OH + \tfrac{1}{2}O_2 \rightarrow HCHO + H_2O \text{ (formaldehyde)}$$

$$HCHO + \tfrac{1}{2}O_2 \rightarrow HCOOH \text{ (formic acid)}$$

When methanol is burned in a cast iron container, the formic acid and methylene hydroxy-peroxide in the residue oxidize the metal and form rust.

In the studies examined, the wear rates with unleaded gasoline and anhydrous ethanol were in the normal range; however, when the ethanol contained 11% water, the wear increased significantly as the engine temperature was reduced. Considerably greater wear rates were observed with anhydrous methanol, and those increased dramatically when the methanol contained 11% water.

Effects of Alcohols on Various Materials

A variety of metals have been identified as potentially sensitive to degradation by methanol/gasoline blends in the range of 10-15% methanol. [8] These include: (a) terne steel, which is used in fuel tanks, (b) magnesium, and (c) aluminum, which is used in carburetors and fuel pump bodies.

Terne steel is a sheet steel that is hot dipped in a tin-lead solution to retard corrosion; it is almost exclusively used in automotive fuel tanks. Uniform corrosion leads eventually to a removal of the protective terne lining the fuel tank, which in turn leads to accelerated corrosion of the fuel tank steel itself. Presence of water contamination leads not only to more uniform corrosion but tends to increase the tendency toward pitting corrosion which can lead to fuel tank perforation in a short period of time. Fleet test results using terne metal in the gas tanks have not shown any catastrophic failure of the tanks due to corrosion by gasoline/methanol blends under 15% methanol.

However, observations of a galvanic corrosion in methanol/gasoline blends has been reported. [9] This is a corrosion due to the presence of electrical currents in methanol/gasoline blends, currents created by rear-mounted fuel pumps. Gasoline is known to be a relatively good electrically insulating liquid due to the general non-polar nature of the constituents hydrocarbons. Methanol, unlike gasoline, is very polar and conducts electricity much better. Therefore, the presence of methanol in a fuel blend would be expected to increase the tendency and extent of galvanic corrosion.

Several non-metals used in fuel systems have been responsible for most reported failures of vehicles fueled with methanol/gasoline blends. These include a large number of different polymers, elastomers, rubbers, plastics, etc. Other investigators have shown no problems in operation of methanol/gasoline blends. [10] Sensitive non-metals include natural rubber (not used in current vehicles), polyurethane (used as fuel lines in some vehicles), cork gasket material, leather, polyester-bonded fiberglass laminate, PVC, and certain other plastics (polyanides and methyl-methacrylate). Non-metals resistant to methanol include Buna N and Neoprene rubber, polyethylene, nylon and polypropylene. Contradictory results have been reported on a very large number of non-metals, including Nitrile and Viton. [11]

The effect of ethanol/gasoline and methanol/gasoline blends on the rate of fuel hose permeation has been investigated. [12] Fuel permeation rate through a fuel hose is a function of several parameters: (1) fuel aromatic content, (i.e., the greater the aromatics by volume, the greater the permeation); (2) hose material type and composition; (3) percent volume of alcohol; and, (4) type of alcohol. With an SAE 30 R 7 hose, 10% ethanol/gasoline blends increase the permeation rate about 25%, while 15% methanol/gasoline blends will increase the permeation rate 63%. Similarly, with an SAE 30 R 8 hose, 10% ethanol/gasoline blend will increase the permeation rate approximately 151%, while a 15% methanol/gasoline blend will increase the permeation rate 342%.

Influence on Fuel Distribution System

When ethanol or methanol, either pure or blended with gasoline, is shipped through a common carrier pipeline, it may loosen some of the deposits which have precipitated out from previous shipments and line the inner surfaces of pipe. This would not only result in contamination of the alcohol/gasoline blend and damage compressors and pressure maintenance units, but might possibly contaminate the next product sent through the pipeline as well. [13] **In contrast, alcohol-based ethers (such as ETBE, MTBE, and TAME) are considered by pipeline operators to be "pipeline-fungible"; that is, they can be shipped in pipelines interchangeably with gasoline and crude oil (without affecting the pipelines or subsequent shipments.**

Vehicle Failures

Experimental and commercial conversions of production vehicles to alcohol fuel have been performed for many years. Brazil instituted a large-scale alcohol fuel program in 1975. More than 11.9 million vehicles have been produced to operate on neat and 22% ethanol blends. In the United States, numerous research reports have been written in the past decade describing the negative effects of neat alcohol and high-level alcohol blends. **The corrosive properties of high-level alcohol blends or neat alcohols necessitate significant modifications to current U.S. vehicle technology.** After only 2 years Brazil was able to overcome almost all problems associated with alcohol fueled vehicles, indicating that the technology is available. Failures reported to date with flexible fuel vehicles (FFV) vehicles designed specifically to accommodate high-level alcohol blends as well as gasoline-based fuels, indicate that further reliability testing is needed if their reliability is to be similar to gasoline fueled cars.

Early Retrofits to Production Vehicles

In 1982 the Bank of America (BOA) converted 416 primarily carbureted vehicles to operate on low concentration blends (up to 18%) as well as neat methanol. The BOA reported negative effects of methanol on elastomers, carburetors, fuel lines, fuel pumps, fuel level sending units, terneplate gas tanks, as well as accelerated wear data from various internal engine components. [14] For further information on failures in older designs, refer to [15].

Maintenance data released by the California Air Resources Board (CARB) show intermittent fuel system problems causing inaccurate emissions measurements. While some changes were due to developmental reasons, the majority of the problems were due to clogging of injectors caused by the corrosive reactions between methanol and various fuel system components. Parts replaced by Ford on their carbureted and fuel injected 1983 Escorts included carburetors, fuel injectors, catalysts, EGR valves, oxygen sensors, fuel pumps, computer chips, and temperature sensors. Two Toyota test vehicles had their fuel injectors replaced twice because of driveability problems before they had logged 25,000 miles. One vehicle experienced engine failure after 43,500 miles. [16]

Current Modifications to Vehicles (M-85)

One U.S. automaker performed the following fuel system modifications to a 1988 production model to prevent the corrosion problems of high-level methanol blends [17],

- Stainless steel fuel tank with stainless flame arrestors in the fill and vent tubes to prevent ignition by an external source.

- Methanol-resistant float level potentiometer with a corrosion protection circuit.

- Higher flow methanol-tolerant fuel injector and fuel pump to handle higher flow rates.

- Stainless fuel lines with accompanying teflon fuel hoses.

- Anodized aluminum fuel injection rail and modified pressure regulator.

In addition, the necessary on-board hardware was provided to change the engine operating parameters to optimize the combustion of M-85. These modifications are typical for conversions of conventional vehicles to high-level alcohol blends.

Lubrication Failures

The use of neat methanol in current engine designs presents lubrication requirements substantially different than those of gasoline. Research has shown that using the same conventional mineral oil used in current engines severely increases upper cylinder bore wear, valve train wear and connecting rod bearing wear [18]:

	Gasoline	Methanol
Valve Train Cam Wear (mils)	0.5	2.7
Cylinder Bore Wear (mils)		
Longitudinal	0.9	9.3
Transverse	2.7	16.1
Connecting Rod Bearing (mg)	63	189

Preliminary experiments have demonstrated the ability of higher quality synthetic oils to reduce the severity of the wear associated with methanol combustion. Further work will be needed on lubrication composition to prevent the conversion of engine oil to an oil/methanol/water emulsion. This breakdown of the oil's lubricating properties is thought to be responsible for the higher wear. [19]

FFV Failures

Data reported by CARB indicate the replacement of original fuel injectors in 1987-1988 Crown Victorias FFVs with an improved injector virtually eliminated the injector fouling problems experienced initially. In addition, the replacement of the fuel pumps with stainless steel units has provided trouble-free operation with the exception of increased noise. Mileage accumulation varies from 23,000-41,000 miles (as of Nov. 1988). [20]

Multi-fuel vehicles utilize sensors to determine the alcohol/gasoline ratio in the particular blend being used. These systems can operate on ethanol as well as methanol blends. Currently there are optic and dielectric type sensors being used by Ford, General Motors, and Chrysler. The previously cited CARB analysis of the Ford Crown Victorias FFVs noted several failures of the cars' optical sensors, indicating the need for more development work in that area.

A recent SAE report describes the errors associated with both measuring systems. The optic sensor has inherently greater error due to the change in refractive index associated with different hydrocarbon constituents and the effect of deposits building on the fuel/optic interface. Although the dielectric measuring technique requires a temperature compensation function for variations in capacitance with respect to temperature, the error associated with this sensor is 5%. [21] The effect of water content on sensor performance is still not known. The authors indicate that both systems need to be further developed to assure durability and reliability.

Additives Required to Prevent Corrosion

Inhibitors and Higher Alcohols

Corrosion inhibitors are used in conventional gasolines to retard corrosion in metal fuel systems components. Higher alcohols, especially C_4 (i.e., iso-butyl or tert-butyl) alcohols, can be used to prevent or minimize phase separation in water-contaminated alcohol/gasoline blends. [22,23] The prevention of phase separation would have definite benefits for overall driveability as well as in corrosion of water-sensitive components such as aluminum.

Acid Neutralizers in Lubricant Oil

One of the functions of an engine oil is to protect surfaces against various chemical attacks. In particular, acids produced during combustion of gasoline/alcohol blends are neutralized by certain oil additives. Examples for acid neutralizers are zinc dialkyl-dithiophosphates and sulfonates, and calcium sulfonate. As seen in Figure 7-2 [24], the use of an acid neutralizer in lubricant oil in methanol-fueled vehicles provides significantly reduced wear but still is twice that of a gasoline engine. More frequent oil changes may be required to overcome this problem.

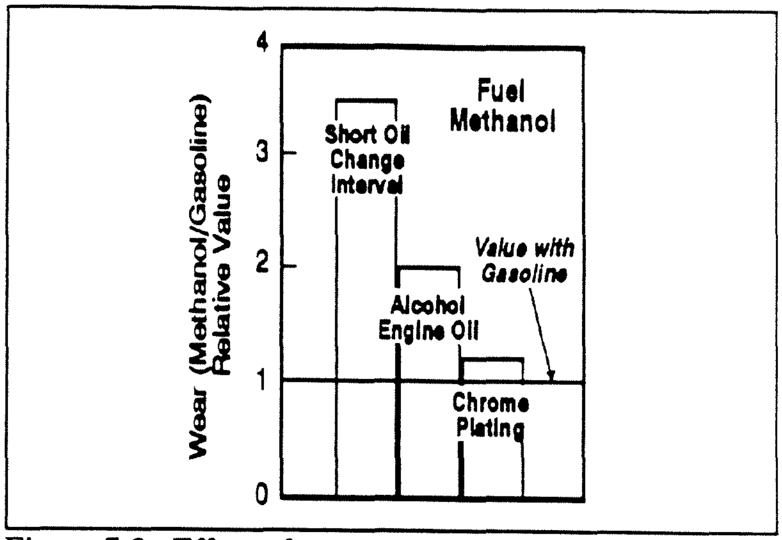

Figure 7-2., Effect of counter-measures on cylinder bore corrosive wear.

Surface Treatment of Engine Parts

By treating the crankshaft with soft nitriding and by plating the cylinder bores with chrome, wear with methanol fuel can be virtually reduced to the level of a gasoline engine (Figure 7-2). The chrome plating was electrically pitted in order to make it sufficiently rough to retain the oil film. [25]

Shorter Lubricant Oil Change Intervals

Although the basic compounds required for preventing oxidization and deterioration are contained in the oil, as the total engine operating hours increases, the basic compounds are neutralized and the lubricant oil shows increased acidity. Experimental results confirm that the main cause for the corrosive wear in methanol-fueled engines is accumulation of formic acid in the lubricant oil. Shorter lubricant oil change intervals reduce corrosive wear significantly, as shown in Figure 7-3. [26]

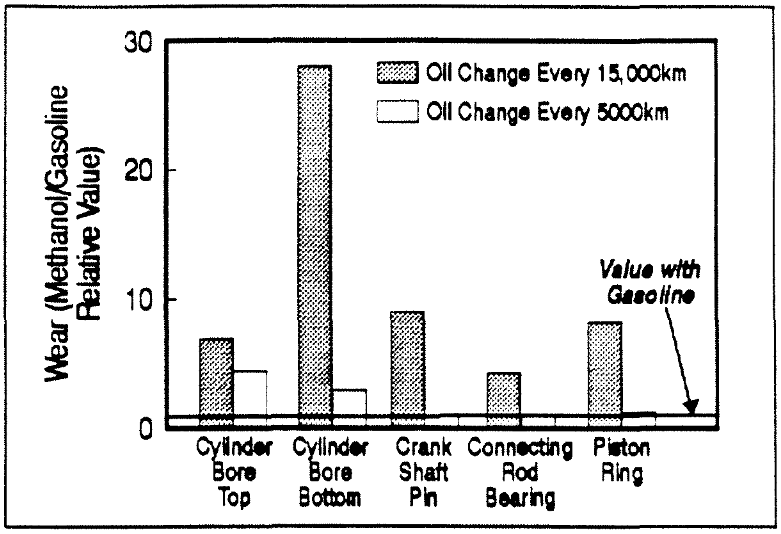

Figure 7-3., Effect of short oil change interval on wear.

ENDNOTES:

1. Heath, M., "Towards a Commercial Future: Ethanol & Methanol as Alternative Transportation Fuels." Canadian Energy Research Institute, The University of Calgary Press, Calgary, January 1989.

2. Otto, K., et al., "A Simple Coupon Test for Analyzing Corrosion Caused by Combustion Products of Liquid Fuels." SAE Paper 880039.

3. Otto, K., et al., "Steel Corrosion by Methanol Combustion Products: Enhancement and Inhibition." SAE paper 861590.

4. Ryan, T. W., III, et al., "Understanding the Mechanism of Cylinder Bore and Ring Wear in Methanol Fueled SI Engines." SAE Paper 861591.

5. Naegeli, D. W., "Combustion-Associated Wear in Alcohol-Fueled Spark Ignition Engines." SAE Paper 891641, 1989.

6. Ichimiya, T., et al., "Wear Mechanisms of Methanol Fueled Engines." SAE Paper 852199.

7. Ibid.

8. Garpe, R. J., "A Review of the Compatibility of Methanol/Gasoline Blends with Motor Vehicle Fuel Systems." Technical Report. EPA/AA/CTAB/PA/81-12, May 1981.

9. Ibid.

10. Ibid.

11. Ibid.

12. Baltz, G. F., "Effects of Alcohol Extended Fuels on the Rate of Fuel Hose Permeation." SAE Paper 880709.

13. Heath, op.cit., 1989.

14. Fisher, M.R., *Vehicle Conversion and Methanol Fuel Program 1980-82*, Bank of America, 1983.

15. EA Mueller, "Status of Alcohol Fuels Utilization Technology for Highway Transportation: A 1986 Perspective," Oak Ridge National Laboratory, Report ORNL/SUB/85-22007/4, 1988.

16. McMahon, W., and Larsen, J., "Alcohol-Fueled Vehicle Fleet Test Program-Ninth Interim Report," California Air Resources Board, Report ARB/MS-89-09, November, 1989.

17. Society of Automotive Engineers, "Methanol Innovation: Technical Details of the 1989 Methanol Marathon," SAE Publication SP-804, 1990.

18. Buck, W.H., Lohvis, J. R., and Murphy, J.A., "Lubrication Studies in a Methanol-Fueled Spark Ignition Engine," SAE Paper 892156, 1989.

19. Schwartz, S. E., Smolenski, D. J., and Clark, S. L., "Energy and Retention of Methanol Fuel in Engine Oil," SAE Paper 880040, 1988.

20. McMahon et. al., op.cit., Appendix B.

21. Schmitz, G. Bartz, R., Hilger, U., and Sieden Top, M. "Intelligent Alcohol Fuel Sensor," SAE 900231, 1990.

22. Lee, H.K., Shah, D.O. and Brinkman, N.D., "Enhancing Low Temperature Phase Stability of a 50/50 Methanol/Hydrocarbon Blend, SAE 881680, 1988.

23. Keller, J. L., et al. "Methanol Fuel Modifications for Highway Vehicle Use." Contract Number EY-76-C-04-3683 (Washington, D.C.; Department of Energy, July 1978).

24. Ichimiya, T., op.cit., et al., 1985.

25. Ibid.

26. Ibid.